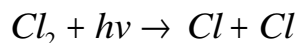


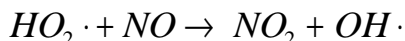
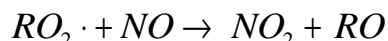
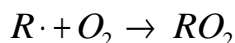
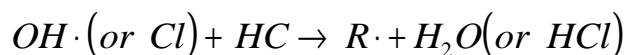
## Chlorine Reaction Mechanism

To simulate the effects of chlorine chemistry, the mechanism developed by Whitten, Johnson, and Killus (1982) was used in this study. Table 8-1 summarizes the chemical reactions, rate constants, and activation energies associated with the chlorine mechanism.

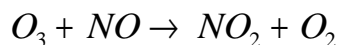
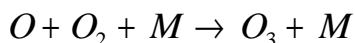
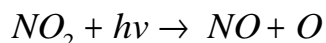
The mechanism developed by Whitten, Johnson, and Killus relies on the presence of hydrocarbons to explain the ozone enhancement effect. As discussed by Whitten and colleagues, elemental chlorine molecules photolyze in sunlight to yield chlorine atoms via the reaction



These chlorine atoms replace many of the hydroxyl radical (OH $\cdot$ ) reactions in the usual smog chemistry. However, the chlorine atom reactions occur at a much faster rate. Moreover, the hydroxyl radical chemistry is also activated, which continues the cycles leading to ozone formation. Briefly, the ozone generation cycle is as follows:



where HC is some hydrocarbon molecule. OH $\cdot$  is generated at the end of either the OH $\cdot$  (or the Cl initiated cycle. Key steps toward ozone generation are the reactions that oxidize NO to NO<sub>2</sub> because such reactions affect the following cycle that is occurring simultaneously:



where M is either O<sub>2</sub> or N<sub>2</sub>. Thus, O<sub>3</sub> can build up by this second cycle whenever NO is converted to NO<sub>2</sub> without the loss of O<sub>3</sub>.

The generation of hydroxyl radicals in photochemical smog involves the photolysis of carbonyls. At typical hydrocarbon and chlorine levels (RHC = 0.4 ppmC, Cl<sub>2</sub> = 0.05 ppm as chloride), chlorine may produce radicals at a rate that is two orders of magnitude greater than carbonyl photolysis. At these concentration levels, hydrocarbon oxidation may be as much as 400 times faster than without chlorine.